# Unexpected Synthesis of a 1,4-Diaza, $2\sigma^3\lambda^3$, $3\sigma^4\lambda^5$ Diphospholene

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The reaction of the dichlorophosphine $(Me_3Si)_2CHPCl_2$ (**1a**), with a trisilylated amidine (**2**), leads to the formation of a 1,4-diaza, $2\sigma^3\lambda^3$, $3\sigma^4\lambda^5$ diphospholene (**3a**), the *X*-ray crystal structure of which has been determined.

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Considerable work has been devoted to the synthesis of various cyclic conjugated P=C or P=N dico-ordinated phosphorus species during the last decade.[1a] Although the chemistry of the corresponding linear conjugated phospha-alkenes is well developed,[1] to our knowledge no linear conjugated phospha-imines have been described so far.

In search of the preparation of such species, we have examined reactions of dichlorophosphines with trisilylated amidines. This communication reports the unexpected formation and the *X*-ray structure determination of the 1,4-diaza, $2\sigma^3\lambda^3$, $3\sigma^4\lambda^5$ diphospholene (**3a**) *via* a [4 + 1] cycloaddition involving a transient conjugated phospha-imine (**5a**).

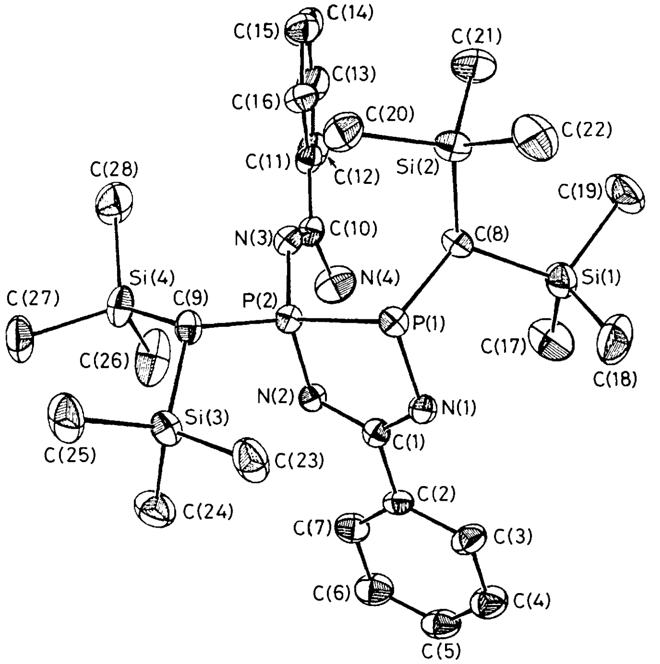
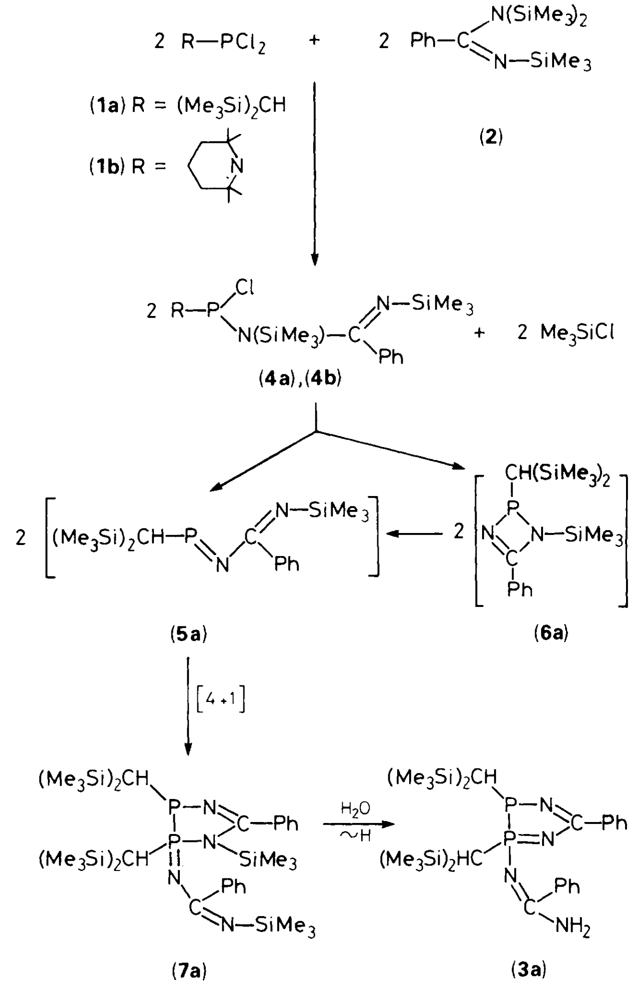


**Figure 1.** Molecular structure of (**3a**). Some selected bond lengths (Å) and angles (°): P(1)–P(2) 2.250(1), P(1)–N(1) 1.693(3), P(2)–N(2) 1.630(3), P(2)–N(3) 1.634(3), N(2)–C(1) 1.361(5), C(1)–N(1) 1.693(3), N(3)–C(10) 1.304(6), N(4)–C(10) 1.338(5); P(2)–P(1)–N(1) 89.5(1), P(1)–P(2)–N(2) 95.4(1), P(1)–N(1)–C(1) 116.1(3), P(2)–N(2)–C(1) 112.6(3), N(1)–C(1)–N(2) 126.3(4).

The diphospholene (**3a**)† is obtained in 60% yield when a dichloromethane solution of bisyldichlorophosphine, $(Me_3Si)_2CHPCl_2$ (**1a**), is added to a dichloromethane solution of the silylated amidine (**2**) (Scheme 1).

Derivative (**3a**) was isolated and characterized by mass spectrometry and elemental analysis. The $^{31}P\{^1H\}$ n.m.r. spectrum showed a pattern with a large phosphorus–phosphorus coupling constant (δ $^{31}$P89.4 and 55.7 p.p.m.; $^1J_{PP}$ 360 Hz), for the AB system. The $^{13}C\{^1H\}$ and $^1$H n.m.r. spectra further support this assumption.

The crystal structure of (**3a**) was clearly established by an *X*-ray diffraction study (Figure 1).‡ The five-membered ring is nearly planar. The P–P distance [2.25(1) Å] compares well with the values found in analogous heterocycles[2] or in classical linear diphosphines. Endocyclic and exocyclic bond distances suggest that the insaturations are delocalized along the $N_1C_1N_2P_2N_3C_{10}N_4$ molecular fragment: intracyclic P–N bonds are shorter [1.630(3) and 1.634(3) Å] than the exocyclic one [1.693(3) Å] and all the C–N bonds lengths [average 1.35(3) Å] are between single and double carbon–nitrogen bond lengths.



**Scheme 1**

A [4 + 1] cycloaddition involving two moles of the hitherto unknown phospha-imine (**5a**) can be reasonably proposed for the formation of (**3a**) (Scheme 1). Only [2 + 1] or [2 + 2] cycloadditions involving iminophosphane R–P=N–R itself with the formation of the 1,2$\sigma^3\lambda^3$, 3$\sigma^4\lambda^5$-azadiphosphiridine (**8**)[3] or 1,3-diaza, 2,4$\sigma^3\lambda^3$ diphosphetidines (**9**),[4] respectively, have been reported so far.

Two pathways can be postulated for the transient generation of (**5a**). Both involve the monophosphorylated amidine (**4a**) as intermediate, which eliminates trimethylsilylchloride to give (**5a**), either directly or *via* an electrocyclic ring opening[5] of adduct (**6a**). Derivative (**7a**) arising from the [4 + 1] cycloaddition of (**5a**) has been spectroscopically characterized (δ $P_1$ 91.4, δ $P_2$ 56.30 p.p.m., $^1J_{PP}$ 362.7 Hz); it slowly rearranges into the final diphospholene (**3a**). It has not yet been possible to isolate or characterize the transient linear or cyclic species (**4a**), (**5a**), or (**6a**). Nevertheless the addition of

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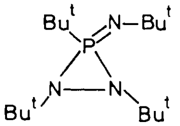
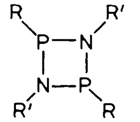
† *Main n.m.r. parameters* for (**3a**): $^{31}$P n.m.r. ($CDCl_3$, 32.44 MHz): δ $P_1$ 89.4, δ $P_2$ 55.7 (ddd, $^1J_{P_1P_2}$ 360, $^2J_{P_1H} = {}^2J_{P_2H} = 27$, $^3J_{P_1H} = {}^3J_{P_2H} = 18.5$ Hz); $^1$H n.m.r. ($CDCl_3$, 80.13 MHz), δ 0.2 (m, 36H, $Me_3Si$), 1.25 [m, 2H, $CH(SiMe_3)_2$], 7.6 (m, 10H, $C_6H_5$), 8.31 (m, 2H, $NH_2$); $^{13}$C n.m.r. ($CDCl_3$, 20.15 MHz): δ 0.45 (d, $^3J_{CP}$ 7.5 Hz, $CH_3$, $SiMe_3$), 1.89 (s, $CH_3$, $SiMe_3$), 2.38 (s, $CH_3$, $SiMe_3$), 2.6 (s, $CH_3$, $SiMe_3$), 12.83 (dd, $^1J_{CP_1}$ 73, $^2J_{CP_2}$ 5.1 Hz, CH–$P_1$), 19.22 (dd, $^1J_{CP_2}$ 51.7, $^2J_{CP_2}$ 14.8 Hz, $CHP_2$), 128 (m, *C*, Ph), 134.55 (d, $^3J_{CP_2}$ 18.50 Hz, $P_2NC$–$C_{ipso}$), 138.34 (dd, Σ $^3J_{CP}$ 22.0 Hz, N=C–$C_{ipso}$), 161.95 (d, $^2J_{CP_2}$ 16.7 Hz, $P_2NCNH_2$), 170.1 p.p.m. (dd, Σ $^2J_{CP}$ 21.6 Hz, $P_1N$–C–$NP_2$).

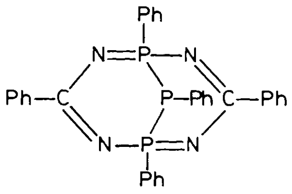
‡ *Crystal data* for $C_{28}H_{50}N_4P_2Si_4$ (**3a**): $M = 617$, monoclinic, $a = 13.18(7)$, $b = 15.61(6)$, $c = 17.89(5)$ Å, $\beta = 96.5(2)°$, $U = 3659$ Å$^3$, space group $P2_1n$, $Z = 4$, $D_c = 1.12$ g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 2.65 cm$^{-3}$. Crystal dimensions 0.4 × 0.5 × 1. Data were measured on an Enraf–Nonius diffractometer with graphite monochromated Mo-$K_\alpha$ radiation using θ/2θ scans. The structure was solved using direct methods and refined anisotropically for all the atoms, hydrogen excepted (only introduced in the calculation after constrained at 0.97 Å to the bonded atoms) without absorption correction, giving $R = 0.038$, $R_w = 0.039$ for 3241 independent measured reflections [$I > 3\sigma(I)$] and 343 independent parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**(8)**



**(9)**



**(10)**

tetramethylpyperidino dichlorophosphine (**1b**) to amidine (**2**) at −40 °C or at room temperature quantitatively leads to the stable monophosphorylated amidine (**4b**).§

In contrast, no clear results are obtained when amidine (**2**) is treated with dimethyl or diethylamino dichlorophosphine, $R_2NPCl_2$ (R = Me or Et). Furthermore, Roesky *et al.*[6] have recently isolated the bicyclic derivative (**10**) by adding three moles of phenyldichlorophosphine to two moles of (**2**). All these results underline the dramatic effect of the phosphorus substituent.

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§ (**4b**) b.p. 90°/0.07 mm. $^{31}$P n.m.r. ($CDCl_3$) $\delta$ 162.6 p.p.m.; *m/z*: 469 ($M^+$).